CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Solvent Proton Nuclear Magnetic Resonance Study of Two Quadridentate Schiff Base Complexes of Nickel(II) in Water and *N*,*N*-Dimethylformamide

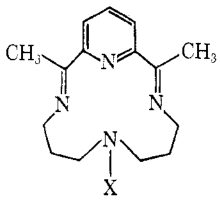
BY L. L. RUSNAK AND R. B. JORDAN*

Received April 19, 1971

The temperature dependences of the solvent water protons and *N*,*N*-dimethylformamide (DMF) formyl proton nmr spectra at 60 and 100 MHz have been measured in the presence of the nickel(II)–Schiff base complexes $NiCR^{2+}$ and $NiCRCH_3^{2+}$. A solvation number of 2 is assumed for all the systems. Chemical exchange effects on the line broadening and chemical shift were observed for both complexes in DMF. The rate constant (sec^{-1}) (25°) for exchange of one solvent molecule, $\Delta H^{\ddagger}$ (kcal mol^{-1}), and $\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1}) are, for $NiCR(DMF)_2^{2+}$, 1.9×10^6, 9.5 (±0.5), −2.2 (±1.0); and for $NiCRCH_3(DMF)_2^{2+}$, 2.8×10^6, 7.8 (±0.5), −2.9 (±2.5). In water only the line broadening shows chemical exchange effects, and in addition the results have a greater but unknown uncertainty because of the difficulty in separating the relaxation mechanisms. For $NiCR(OH_2)_2^{2+}$ in water a combination of line broadening and chemical shift results gives a water proton exchange rate constant (25°) of 4.5×10^4 sec^{-1}, with $\Delta H^{\ddagger} = 6.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14.4$ cal mol^{-1} deg^{-1}. The behavior of $NiCRCH_3(OH_2)_2^{2+}$ was similar to that of $NiCR(OH_2)_2^{2+}$ except that no chemical shift was observed. The activation enthalpy for exchange is found to be 6.3 kcal mol^{-1}; and a chemical shift estimated by analogy to $NiCR(OH_2)_2^{2+}$ gives $k \approx 5 \times 10^4$ sec^{-1} and $\Delta S^{\ddagger} \approx -16$ cal mol^{-1} deg^{-1}. In all cases a frequency dependence of the proton relaxation time in the first coordination sphere of the metal complex was observed. This behavior is interpreted in terms of a magnetic field dependence of the electron spin relaxation time.

Introduction

The nmr line broadening method has been extensively applied to the determination of ligand exchange rates on nickel(II).[1] The exchange behavior of many hexasolvated systems has been studied, and recently attention has focused on the effect of nonexchanging ligands on the solvent ligand exchange rates.[2–4] This report presents the results of such a study on the nickel(II) complexes of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (Ia) and its methylated analog (Ib). The complexes will be referred to as $NiCR^{2+}$ and $NiCRCH_3^{2+}$, respectively.



Ia, X = H
b, X = CH_3

These complexes exist as tetragonally distorted pseudooctahedral species in coordinating solvents. This geometry is widely observed in biologically important metal ion complexes, but there is relatively little kinetic information on such systems. Kluiber, *et al.*,[5,6] have studied the rate of complexing of bis(β-diketonate)-nickel(II) complexes with picoline derivatives and found that the rates could be understood in terms of steric interactions.

Previous work has shown that $NiCR^{2+}$ and $NiCRCH_3^{2+}$ undergo a rapid diamagnetic–paramagnetic equilibrium, represented in general by

$$\underset{\text{diamagnetic}}{NiA_4^{2+}} + 2(\text{solvent}) \rightleftharpoons \underset{\text{paramagnetic}}{NiA_2(\text{solvent})_2^{2+}}$$

The temperature dependence of this equilibrium has been measured in various solvents.[7] These results are used here to correct the nmr results for the presence of the inactive diamagnetic species.

Experimental Section

The preparation and characterization of the various $NiCR^{2+}$ and $NiCRCH_3^{2+}$ salts have been described previously.[7]

The samples in DMF were prepared under vacuum using doubly vacuum-distilled solvent which was stored over molecular sieves. Samples were prepared by distilling DMF onto a known weight of nickel complex in a suitable weighed container. The container plus solvent was reweighed to determine the amount of solvent. An appropriate amount of the solution was poured into an nmr tube under vacuum. Then cyclopentane for use as an internal standard was vacuum distilled into the nmr tube and the sample sealed off.

The chemical shift and line broadening were shown to depend directly on the $NiCR(PF_6)_2$ concentration in DMF for five samples in the concentration range 6.56×10^{-2} to 8.63×10^{-1} *m* at 50°. Variable-temperature studies on DMF solutions of $NiCR(PF_6)_2$ were performed on four samples in the concentration range 1.24×10^{-1} to 5.55×10^{-1} *m*. In addition three samples of 1.31×10^{-1}, 2.24×10^{-1}, and 2.71×10^{-1} *m* $NiCR(ClO_4)_2$ were studied to check for any anion or possible fluoride ion effects in the PF_6^- salt. The results from both salts were identical within the experimental error and the data from all seven samples were analyzed together.

Only the perchlorate salt of $NiCRCH_3^{2+}$ was studied in DMF. Five samples in the concentration range 4.68×10^{-2} to 2.93×10^{-1} *m* were used.

The aqueous solutions were not prepared under vacuum. Five samples of $NiCR(BF_4)_2$ were studied over the concentration range 0.280–0.520 *m*. Samples of the perchlorate salt were found to give identical results. Three samples of 0.326, 0.376, and 0.444 *m* $NiCRCH_3(BF_4)_2$ were used. The perchlorate salt of the last was too insoluble in water to be studied. Solutions were unbuffered at pH ~4. Two samples of $NiCR^{2+}$, adjusted to pH 1.6 and 7.6, showed no difference in line broadening.

Sodium 3-trimethylsilyl-1-propanesulfonate (DSS) was used as an internal standard in water for the work at 60 MHz. Since the most intense resonance from DSS was too weak to give a good

---

(1) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967).

(2) M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

(3) D. Rablen and G. Gordon, *Inorg. Chem.*, **8**, 395 (1969).

(4) J. E. Letter, Jr., and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 864 (1971).

(5) R. W. Kluiber, R. Kukla, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 1319 (1970).

(6) R. W. Kluiber, F. Thaller, R. H. Low, and W. DeW. Horrocks, Jr., *ibid.*, **9**, 2592 (1970).

(7) L. L. Rusnak and R. B. Jordan, submitted for publication in *Inorg. Chem.*

lock signal, either acetone or *tert*-butyl alcohol was used at 100 MHz. The latter samples were checked at 60 MHz and no effect of the internal standard was observed at the concentration employed (~5% by volume).

The nmr spectra were obtained on Varian Associates A-56/60 and HA-100 spectrometers equipped with standard temperature control units. Temperatures on the A-56/60 were determined by comparison of the chemical shifts in pure methanol and ethylene glycol to calibration charts provided by Varian Associates. Temperatures on the HA-100 were measured with a copper–constantan thermocouple. It has been observed, in this and previous work, that when the observations are frequency independent, the results from the two spectrometers agree within the error of measurement.

Results and Treatment of Data

The solvent proton nmr line broadening caused by the paramagnetic ion may be expressed in terms of the relaxation time T_{2P}, defined by

$$(T_{2P}P_M)^{-1} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{solv})}{P_M} \qquad (1)$$

where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the full line widths at half-height in the presence and absence, respectively, of the paramagnetic species. P_M is the ratio of solvent bound to the paramagnetic species to the free-solvent concentration. It has been shown previously[7] that both $NiCR^{2+}$ and $NiCRCH_3{}^{2+}$ undergo a temperature-dependent diamagnetic–paramagnetic equilibrium. Therefore

$$P_M = \frac{nX_P[Ni^{2+}]_{total}}{S_0 - nX_P[Ni^{2+}]_{total}} \qquad (2)$$

where n is the number of the solvent molecules in the first coordination sphere of the nickel complex, S_0 is the molal solvent concentration in the pure solvent, and X_P is the mole fraction of the nickel complex in the paramagnetic form. The latter may be calculated since

$$\frac{X_P}{1 - X_P} = \exp\left(\frac{-\Delta H° + T\Delta S°}{RT}\right) \qquad (3)$$

Values of $\Delta H°$ and $\Delta S°$ have been determined for each system as described previously.[7]

A value of 2 has been assumed for n, implying a pseudooctahedral structure for the paramagnetic species. Indirect evidence supporting this assumption has been presented previously.[7] However, if n is actually 1, the general interpretation presented here would not be affected, since the second term in the denominator of eq 2 is small. The calculated exchange rates and coupling would increase by a factor of 2, and $\Delta S^{\ddagger}$ would increase by 1.4 cal mol^{-1} deg^{-1}.

The factors affecting $(T_{2P}P_M)^{-1}$ may be considered in terms of the equation

$$(T_{2P}P_M)^{-1} = \frac{1}{\tau_M}\left\{\frac{T_{2M}{}^{-2} + (\tau_M T_{2M})^{-1} + \Delta\omega_M{}^2}{(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M{}^2}\right\} + T_{2O}{}^{-1} \qquad (4)$$

This is the expression given by Swift and Connick[8] only modified by the addition of the outer-sphere contribution $T_{2O}{}^{-1}$. The other symbols have their usual meanings. The temperature dependences of the various terms in eq 4 are assumed to take the forms

$$\tau_M{}^{-1} = \frac{kT}{h}\exp\left(\frac{-\Delta H^{\ddagger} + T\Delta S^{\ddagger}}{RT}\right) \qquad (5)$$

$$T_{2M}{}^{-1} = C_M \exp(E_M/RT) \qquad (6)$$

$$T_{2O}{}^{-1} = C_O \exp(E_O/RT) \qquad (7)$$

and

$$\Delta\omega_M = -\left(\frac{A}{\hbar}\right)\frac{\omega_0\mu_{eff}\beta\sqrt{S(S+1)}}{3kT\gamma_I} \qquad (8a)$$

$$= -\frac{C_\omega}{T} \qquad (8b)$$

The first expression for $\Delta\omega_M$ is that given by Bloembergen,[9] and the second is simply obtained with the added assumption that μ_{eff} is independent of temperature.

The chemical shift of the bulk solvent resonance ($\Delta\omega_{obsd}$) caused by the paramagnetic ion is given by

$$\Delta\omega_{obsd}/P_M = \frac{-\Delta\omega_M}{((\tau_M/T_{2M}) + 1)^2 + (\tau_M\Delta\omega_M)^2} \qquad (9)$$

Measurements of the chemical shifts provide an independent method of determining the solvent exchange rate parameters especially when $(\tau_M\Delta\omega_M)^2$ is of the order of 1. The chemical shifts can also provide a value for $\Delta\omega_M$ since in the limit of fast exchange $\Delta\omega_{obsd}/P_M = -\Delta\omega_M$. The $\Delta\omega_{obsd}$ values are not useful however in determining C_M or E_M due to the difficulty of resolving T_{2M} from τ_M.

It should also be noted, that in the fast-exchange limit, the temperature dependence of the measured shifts provides a qualitative assessment of the validity of the corrections which have been made for the diamagnetic–paramagnetic equilibrium. If the data are improperly corrected, an unreasonably large shift would be found at $T^{-1} = 0°K^{-1}$.

$NiCR(PF_6)_2$ in N,N-Dimethylformamide.—The temperature dependences of $(T_{2P}P_M)^{-1}$ and $(\Delta\omega_{obsd}/P_M)$ for the formyl proton are shown in Figures 1 and 2, respectively. All experimental points have been corrected for the formation of diamagnetic species using, in eq 3, the previously determined values of −3.27 kcal mol^{-1} and −7.7 cal mol^{-1} deg^{-1} for $\Delta H°$ and $\Delta S°$, respectively. It may be noted that below −40° the

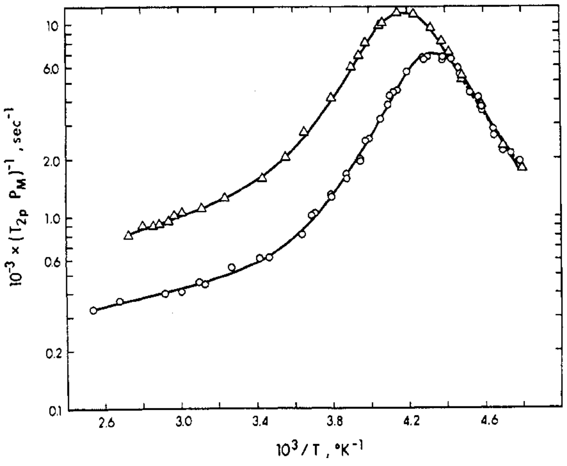


Figure 1.—Temperature dependence of $-\log(T_{2P}P_M)$ for the formyl proton in DMF solutions of $NiCR(PF_6)_2$: ○, 60 MHz; △, 100 MHz.

---

(8) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(9) N. Bloembergen, *ibid.*, **27**, 595 (1957).

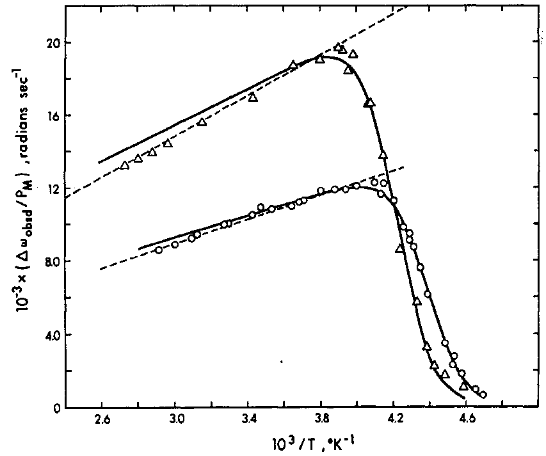


Figure 2.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the formyl proton in DMF solutions of $NiCR(PF_6)_2$: ○, 60 MHz; Δ, 100 MHz. The significance of the dashed and solid curves is explained in the text.

complex is >96% paramagnetic and the corrections are quite small; however at 120° the correction is quite significant since the complex is 57% in the paramagnetic form.

The temperature dependence of $(T_{2P}P_M)^{-1}$, shown in Figure 1, is typical of that observed for other nickel(II) systems. The value of $(T_{2P}P_M)^{-1}$ is primarily controlled successively by T_{2M}^{-1}, $\tau_M\Delta\omega_M^2$, and finally τ_M^{-1} as the temperature is lowered. The results have been fitted to eq 4 with certain restrictions applied to the parameters as given in Table I. It should be noted that no T_{2O}^{-1} contribution is actually observed at low temperatures but analysis of the data for this system and that of $NiCRCH_3^{2+}$ in DMF permitted the outer-sphere term to be estimated. The results for $Ni(DMF)_6^{2+}$ in DMF were also useful in this connection.

Table I

Least-Squares Best-Fit Parameters for $NiCR(PF_6)_2$ in DMF

	$(T_{2P}P_M)^{-1}$ data				$\Delta\omega_{obsd}$ data	
	60	100 MHz			60	100
	MHz	A	B	C	MHz	MHz
$\Delta H^{\ddagger}$, kcal mol^{-1}	9.63	9.18	9.63	9.63	9.52	9.80
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	2.71	0.24	2.17	2.10	2.66	3.18
$10^{-6}C_\omega$, radians sec^{-1} deg	3.08[a]	5.36	5.14[d]	5.14[d]	3.08	5.14
$E_M = E_O$, kcal mol^{-1}	1.06[b]	1.06	1.06[e]	1.42	1.06[e]	1.06[e]
C_M, sec^{-1}	64.0[c]	148.6	148.9	87.0	64.0[f]	148.9[g]
C_O, sec^{-1}	19.6[c]	47.1	45.65	26.7	...	...

[a] Various five-parameter fits gave C_ω between 3.04×10^6 and 3.17×10^6 depending on what C_O or E_M was chosen. The value tabulated was determined from $\Delta\omega_{obsd}$ analysis and held constant in this fit. [b] Held constant at the value given by the 100-MHz fit A. When allowed to vary, E_M was in the range 1.1–1.3 kcal mol^{-1} depending on the C_O value used. [c] The ratio of C_M to C_O was held constant at 3.26 as indicated by the 100-MHz fit B. This is consistent with values of ~3 obtained for $Ni(DMF)_6^{2+}$ in DMF and $NiCRCH_3(DMF)_2^{2+}$ in DMF. [d] Held constant at values indicated by the 60-MHz shift to test for consistency of 60- and 100-MHz data. $\Delta H^{\ddagger}$ was fixed as indicated by the 60-MHz $(T_{2P}P_M)^{-1}$ data. [e] Held constant at the value from fit A. [f] Held constant at the value from the 60-MHz fit. [g] Held constant at the value from fit B.

This system is unusual, however, in that the T_{2M}^{-1} value is frequency dependent. It is apparent in Figure 1 that although T_{2M}^{-1} is the major contribution to $(T_{2P}P_M)^{-1}$ for $T^{-1} \lesssim 3.4 \times 10^{-3}$ °K^{-1}, the 60- and 100-MHz data do not converge above this temperature. This behavior has been observed generally for $NiCR^{2+}$ and is attributed to a frequency dependence of the correlation time controlling the T_{2M}^{-1} relaxation. This will be discussed in general in a separate section of this paper. It has been assumed that the outer-sphere relaxation has the same frequency dependence.

The $\Delta\omega_{obsd}/P_M$ data have been fitted to eq 9 with the assumption that eq 8b is obeyed and taking the parameters for T_{2M}^{-1} from the $(T_{2P}P_M)^{-1}$ fit. The results are shown in Table I and the smooth curves calculated from these parameters are drawn in Figure 2. It should be noted that the predicted values are higher than the observed at higher temperatures. This discrepancy may be due to an error in correcting for the diamagnetic form or to a non-Curie dependence of the chemical shift. Since the maximum discrepancy is only 8%, it is not possible to decide between these alternatives. It is gratifying to find that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the shift data are in good agreement with values from the line broadening results.

Comparison of the values in Table I indicates that the kinetic parameters for DMF exchange can be reasonably given as $\Delta H^{\ddagger} = 9.5 \pm 0.5$ kcal^{-1} mol^{-1} and $\Delta S^{\ddagger} = 2.2 \pm 1.0$ cal mol^{-1} deg^{-1}. These are the average values from the fits in which both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were allowed to vary. Using the value of $C_\omega = 3.08 \times 10^6$ at 60 MHz and assuming $\mu_{eff} = 3.00$ BM,[7] then the hyperfine coupling constant for the CH proton is calculated from the downfield shift to be 2.30×10^6 radians sec^{-1}.

$NiCRCH_3(ClO_4)_2$ in *N*,*N*-Dimethylformamide.—The temperature dependences of $(T_{2M}P_M)^{-1}$ and $\Delta\omega_{obsd}/P_M$ for the CH proton in this system are shown in Figures 3 and 4, respectively. The values given have been corrected for the formation of diamagnetic species using $\Delta H° = -4.85$ kcal mol^{-1} and $\Delta S° = -12.55$ cal mol^{-1} deg^{-1}. This correction is negligible at temperatures below −25° but increases from 3 to 52% as the temperature increases from −25 to +115°.

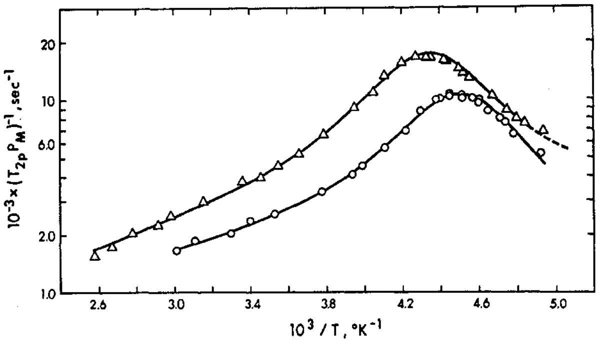


Figure 3.—Temperature dependence of $-\log(T_{2P}P_M)$ for the formyl proton in DMF solutions of $NiCRCH_3(ClO_4)_2$: ○, 60 MHz; Δ, 100 MHz.

The results are qualitatively similar to those for $NiCR^{2+}$ in DMF except that the T_{2M}^{-1} controlled relaxation at high temperature is a more dominant term; therefore the $\tau_M\Delta\omega_M^2$ controlled region is not as well defined. As a result it is not possible to obtain a good value of C_ω from the $(T_{2P}P_M)^{-1}$ data and the value obtained from the chemical shift measurements has been used in all the $(T_{2P}P_M)^{-1}$ fits summarized in Table II.

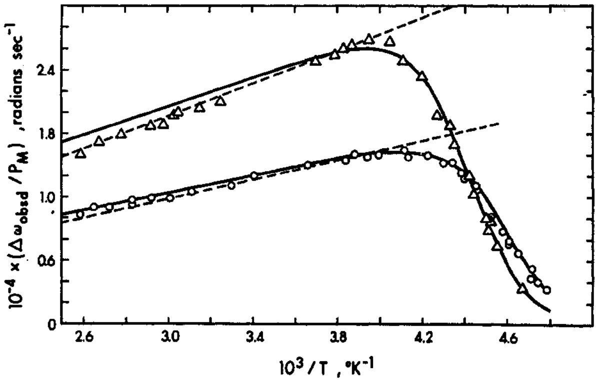


Figure 4.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the formyl proton in DMF solutions of $NiCRCH_3(ClO_4)_2$: ○, 60 MHz; Δ, 100 MHz.

TABLE II
LEAST-SQUARES BEST-FIT PARAMETERS FOR $NiCRCH_3(ClO_4)_2$ IN DMF

	$(T_{2P}P_M)^{-1}$ data		$\Delta\omega_{obsd}$ data		
	60 MHz	100 MHz	60 MHz	100 MHz	
$\Delta H^{\ddagger}$, kcal mol^{-1}	7.84	7.86	8.15	7.24	7.84[c]
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	−2.84	−3.08	−0.65	−5.17	−2.52
$10^{-6} C_\omega$, radians sec^{-1} deg	4.06[a]	6.77	4.06	6.86	6.86
$E_M = E_O$, kcal mol^{-1}	1.35	1.77	1.35[c]	1.77[c]	1.77[c]
C_M, sec^{-1}	162.2	126.3[b]	162.2[c]	126.3[c]	126.3[c]
C_O, sec^{-1}	53.4	41.5[b]	...	...	...

[a] Held constant at the value from the 60-MHz $\Delta\omega_{obsd}$ fit. [b] The ratio of C_M to C_O was held constant at the value from the 60-MHz data. [c] Held constant at the value determined from the appropriate $(T_{2P}P_M)^{-1}$ data.

It should also be noted that in the low-temperature region the data from the 60- and 100-MHz studies do not converge as would be expected for τ_M^{-1} control of $(T_{2P}P_M)^{-1}$. This result is simply due to the frequency dependence of the outer-sphere relaxation which is significant but not dominant when $T^{-1} > 4.6 \times 10^{-3}$ °K^{-1}. As in the case of $NiCR^{2+}$ it has been found that E_M appears larger at 100 MHz than at 60 MHz. The use of the best fit value of E_M from the 60-MHz data for the 100-MHz data or *vice versa* leads to significantly poorer fit and poorer agreement between the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from the two sets of data. This apparent frequency dependence of E_M will be discussed separately in connection with the frequency dependence of T_{2M}.

The chemical shift data were fitted as described in the previous section. Assuming a Curie-law temperature dependence, however, the results actually appear to extrapolate to a shift of −520 Hz (dashed line in Figure 4) rather than zero when $T^{-1} = 0$°K^{-1}. Again this discrepancy might indicate non-Curie behavior or may be due to slight undercorrection for the diamagnetic–paramagnetic equilibrium. In any case the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not significantly affected because the value of $\Delta\omega_M$ extrapolated in the region $T^{-1} = 4.6 \times 10^{-3}$ to 4.7×10^{-3}°K^{-1} is relatively insensitive to the assumed shift at $T^{-1} = 0$°K^{-1}.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the shift and line broadening data are in good agreement. The average values from the fits in Table II are $\Delta H^{\ddagger} = 7.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.93 \pm 2.5$ cal mol^{-1} deg^{-1}. A value of 3.03×10^6 radians sec^{-1} is obtained for the hyperfine coupling constant from both the 60- and 100-MHz chemical shift results, assuming that $\mu_{eff} = 3.00$ BM.

$NiCR(BF_4)_2$ and $NiCRCH_3(BF_4)_2$ in Water.—The line broadening and chemical shift results, corrected for the diamagnetic–paramagnetic equilibrium, are given in Figures 5–7. The corrections were made using $\Delta H° = -6.39$ kcal mol^{-1} and $\Delta S° = -17.9$ cal mol^{-1} deg^{-1}

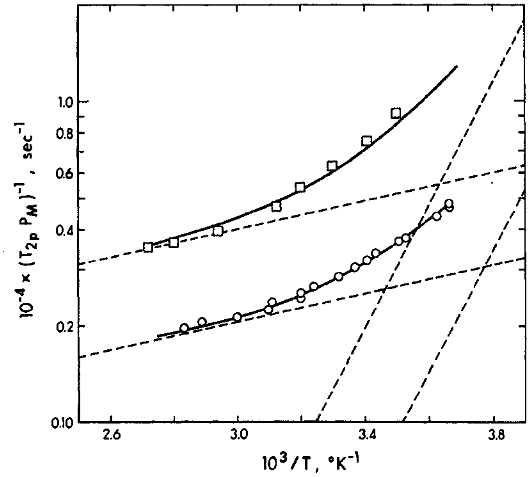


Figure 5.—Temperature dependence of $-\log (T_{2P}P_M)$ in aqueous solutions of $NiCR(BF_4)_2$: ○, 60 MHz; □, 100 MHz. The dashed lines represent the magnitude of the two contributing processes.

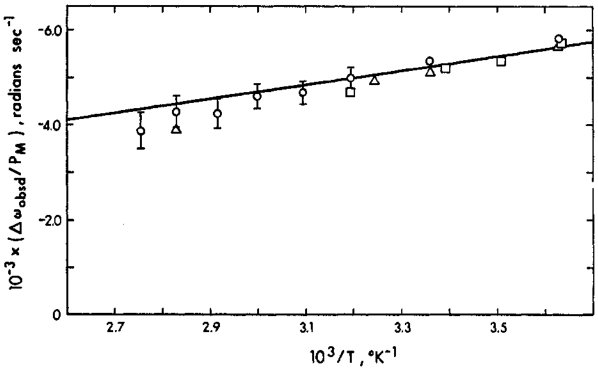


Figure 6.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ at 60 MHz in aqueous solutions of $NiCR(BF_4)_2$. The results of a ±0.5-Hz error in the measured shifts are indicated.

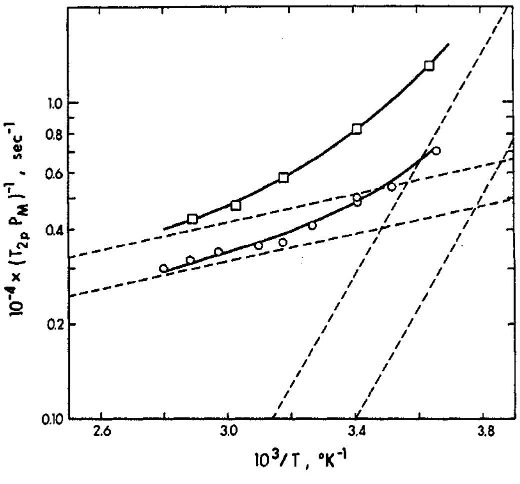


Figure 7.—Temperature dependence of $-\log (T_{2P}P_M)$ in aqueous solutions of $Ni(CRCH_3)(BF_4)_2$: ○, 60 MHz; □, 100 MHz.

for $NiCR^{2+}$ and $\Delta H° = -4.58$ kcal mol^{-1} and $\Delta S° = 15.3$ cal mol^{-1} deg^{-1} for $NiCRCH_3^{2+}$.

It should be noted that no chemical shift was observed in the $NiCRCH_3^{2+}$ system. This result is probably largely due to the smaller percentage of paramagnetic species (52% *vs.* 81% at 25° in $NiCRCH_3^{2+}$ compared to $NiCR^{2+}$). Thus the observed shifts of 3–9 Hz in the $NiCR^{2+}$ system would be less than 5 Hz for $NiCRCH_3^{2+}$ even if the hyperfine coupling constants were the same.

The temperature dependence of $(T_{2P}P_M)^{-1}$ in water is generally similar to that in DMF; however no τ_M^{-1} controlled region is observed because of the more limited liquid range in water.

The results for $NiCR^{2+}$ in water have been analyzed with the equation

$$(T_{2P}P_M)^{-1} = T_{2M}^{-1} + \tau_M\Delta\omega_M^2 + T_{2O}^{-1} \quad (10)$$

which results from eq 4 under the limiting conditions τ_M^{-2}, $(T_{2M}\tau_M)^{-1} \gg T_{2M}^{-2}$. The value of C_ω was fixed at -1.50×10^6 as determined from the measured chemical shift. If μ_{eff} is 3.0 BM, then $A/\hbar = -1.1 \times 10^6$ radians sec^{-1}. The value of $E_O = E_M$ was held constant at 1.0 kcal mol^{-1}. The least-squares fit of the 60-MHz data gave $\Delta H^{\ddagger} = 6.81$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.2$ cal mol^{-1} deg^{-1}, and $(C_M + C_O) = 454.8$ sec^{-1}. The 100-MHz data were fitted with C_ω, $E_O = E_M$, and $\Delta H^{\ddagger}$ held constant at -2.50×10^6 radians sec^{-1} deg, 1.0 kcal mol^{-1}, and 6.81 kcal mol^{-1}, respectively, and $\Delta S^{\ddagger}$ and $(C_M + C_O)$ varied to give best-fit values of -14.5 cal mol^{-1} deg^{-1} and 886.4 sec^{-1}, respectively. The good agreement between the $\Delta S^{\ddagger}$ values is at least partly fortuitious but provides some justification for the assumptions used.

The behavior of $(T_{2P}P_M)^{-1}$ for $NiCRCH_3^{2+}$ in water is very similar to that of $NiCR^{2+}$. However in this case no significant chemical shifts could be detected; therefore C_ω could not be determined and the exchange rate parameters cannot be extracted from the results. If it is assumed that the ratio of C_ω for $NiCR^{2+}$ to $NiCRCH_3^{2+}$ is the same in water and DMF, then the 60- and 100-MHz data can be fitted with $\Delta H^{\ddagger} = 6.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -15.8$ cal mol^{-1} deg^{-1}, and $E_M = 1.0$ kcal mol^{-1}. The value of $(C_M + C_O)$ is 6.97×10^2 and 9.29×10^2 sec^{-1} at 60 and 100 MHz, respectively. These parameters were estimated by graphical fit of the data and are only included to show that the absence of observed shift does not necessarily imply any unusual difference between $NiCR^{2+}$ and $NiCRCH_3^{2+}$ in water.

It should be noted that for the aqueous systems an alternative explanation based only on T_{2M}^{-1} control of $(T_{2P}P_M)^{-1}$ is possible in principle. However detailed consideration of this mechanism given in the following section indicates that this possibility will not quantitatively explain the results.

Magnetic Field Dependence of T_{2M} and T_{2O}.—All of the systems studied in this work have been found to show a field dependence of the T_{2M} relaxation time for the solvent protons in the first coordination sphere of the metal ion. There is also a strong indication that this occurs in the second and higher or outer coordination spheres. Previous work[1] has not indicated such a phenomenon for Ni(II) and some detailed explanation seems to be required.

Proton nuclear relaxation in a paramagnetic system is usually controlled either by the electron–nuclear spin dipole–dipole interaction or by the electron–nuclear hyperfine or scalar interactions.[10,11] These contributions to T_{2M}^{-1} are given by the first and second terms in the equation

$$T_{2M}^{-1} = \frac{1}{15}\,\frac{S(S+1)\gamma_I^2 g^2\beta^2}{r_i^6}\,f_D(\tau_D) + \frac{1}{3}S(S+1)\left(\frac{A}{\hbar}\right)^2 f_e(\tau_e) \quad (11)$$

where γ_I is the nuclear magnetogyric ratio, r_i is the electron–nucleus interaction distance, $A/\hbar$ is the electron–nuclear hyperfine coupling constant, and[12,13]

$$f_D(\tau_D) = 7\tau_{D1} + \frac{13\tau_{D2}}{1 + \omega_S^2\tau_{D2}^2} \quad (12)$$

$$f_e(\tau_e) = \tau_{e1} + \frac{\tau_{e2}}{1 + \omega_S^2\tau_{e2}^2} \quad (13)$$

An expression for the outer-sphere relaxation time, T_{2O}, has been developed by Luz and Meiboom[14] and may be given as

$$T_{2O}^{-1} = \frac{4.14 \times 10^{13}S(S+1)}{d_O^3}\,\rho f_D(\tau_D)\,\frac{S_0}{n} \quad (14)$$

where ρ is the density of the solution and d_O is the distance of closest approach of the proton in the second coordination sphere.

It should be noted that if the correlation times in these expressions are field independent, the T_{2M}^{-1} should decrease on changing from an nmr operating frequency of 60 to 100 MHz, since ω_S changes from 2.48×10^{11} to 4.14×10^{11} radians sec^{-1}. Since the opposite effect was observed in this work, it must be concluded that the correlation times are field dependent.

The correlation times are given by

$$\tau_{D1}^{-1} = \tau_{e1}^{-1} + \tau_r^{-1} = (T_{1e}^{-1} + \tau_M^{-1}) + \tau_r^{-1} \quad (15)$$

$$\tau_{D2}^{-1} = \tau_{e2}^{-1} + \tau_r^{-1} = (T_{2e}^{-1} + \tau_M^{-1}) + \tau_r^{-1} \quad (16)$$

where τ_r is the rotational correlation time for the paramagnetic ion, T_{1e} and T_{2e} are the electron spin longitudinal and transverse relaxation times, respectively, and τ_M has been defined previously. Only T_{1e} and T_{2e} in eq 15 and 16 can be frequency dependent. For an electron spin system with $S = 2$, following McLachlan[15]

$$T_{1e}^{-1} = C_e\left\{\frac{\tau_c}{1 + \omega_S^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_S^2\tau_c^2}\right\} \quad (17)$$

$$T_{1e}^{-1} = \frac{C_e}{2}\left\{3\tau_c + \frac{5\tau_c}{1 + \omega_S^2\tau_c^2} + \frac{2\tau_c}{1 + 4\omega_S^2\tau_c^2}\right\} \quad (18)$$

It should be noted that these equations have been developed with the assumption that $\tau_c < T_{1e}$, which appears not to be valid for the systems being considered here. It seems likely that the functional form of the frequency dependence will be given by eq 17 and 18, but complete quantitative agreement need not be expected. It is encouraging to note that eq 17 predicts a maximum ratio of 2.78 for relaxation times at 60 and 100 MHz and

---

(10) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

(11) N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).

(12) R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966).

(13) The approximation $\omega_I^2\tau^2 \ll 1$ has been used in eq 12 and 13, where ω_I is the resonance frequency of the nucleus being observed.

(14) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(15) A. D. McLachlan, *Proc. Roy. Soc., Ser. A*, **280**, 271 (1964).

this ratio is never exceeded for the systems studied here.

In evaluating the results in terms of these equations there are four unknowns, τ_c, τ_r, C_e, and d_O or r_i, and two experimental numbers, the relaxation times at 60 and 100 MHz. Calculations indicated that only the terms containing τ_{D1} and τ_{e1} are significant in eq 12 and 13, and therefore the ratio of the relaxation times limits τ_c and C_e to within a factor of 10. Previous results provide some guide to reasonable values of τ_r, d_O, and r_i.

An iterative procedure was used to determine τ_c, C_e, d_O, and r_i using the ratio of the relaxation times at the two frequencies as a preliminary guide. The results are summarized in Table III along with the observed and calculated T_{2M} contributions at 25°. Values of r_i and d_O are generally larger than those obtained for hexasolvated metal ions but this may not be unreasonable for a tetragonally distorted complex with a large Schiff base ligand. The longer interaction distances for $NiCRCH_3^{2+}$ compared to $NiCR^{2+}$ would not be unreasonable if the methyl group in the former is exerting some steric influence. The values of τ_c are about a factor of 2 shorter than the τ_r values of 4.5 × 10^{-11} and 11.5 × 10^{-11} sec^{-1} determined from an analysis of the epr spectrum of the vanadyl ion in water and DMF, respectively.[16] On the whole the values are more reasonable than might have been expected considering the approximate nature of the theory.

TABLE III

PARAMETERS AND RESULTS OF $T_{2O}{}^a$ AND $T_{2M}{}^a$ CALCULATIONS

	DMF		H_2O	
	$NiCR^{2+}$	$NiCRCH_3^{2+}$	$NiCR^{2+}$	$NiCRCH_3^{2+}$
$10^{-2}T_{2O}^{-1}$ 60 MHz	1.18	5.19	6.15	9.43
$10^{-2}T_{2O}^{-1}$ 100 MHz	2.74	8.24	12.0	12.6
d_O, Å	5.75	5.80	4.65	4.86
$10^{-2}(T_{2M}^{-1})_{obsd}$				
60 MHz	3.83	15.8	18.5	28.3
100 MHz	8.92	25.1	36.0	37.7
$10^{-2}(T_{2M}^{-1})_{calcd}{}^b$				
60 MHz	3.83	15.8	18.5	28.9
100 MHz	9.11	27.8	35.7	37.7
$10^{-2}(T_{2M})_{hf}{}^c$				
60 MHz	0.23	2.93	0.097	0.11
100 MHz	0.67	8.08	0.27	0.18
$10^{11}\tau_c$. sec	5.80	5.80	1.75	1.00
$10^{11}T_{1e}$, sec (60 MHz)	0.65	4.7	0.415	0.918
$10^{13}T_{2e}$, sec (60 MHz)	0.42	3.0	2.6	14.4
$10^{22}C_e$, sec^{-2}	27.5	3.8	13.4	3.68
r_i, Å	3.94	4.10	2.80	2.86

[a] T_{2M} and T_{2O} values are given in seconds. [b] Sum of the dipolar and hyperfine contributions calculated from eq 11. [c] The hyperfine or scalar contribution calculated using $A/\hbar$ values given in the text.

It was pointed out previously that the temperature dependence of $(T_{2P}P_M)^{-1}$ in the aqueous systems might be explained solely by a T_{2M} relaxation process. This could result since approximately

$$(T_{2P}P_M)^{-1} = T_{2M}^{-1} \propto T_{1e} \propto \left(\frac{1 + \omega_S{}^2\tau_c{}^2}{\tau_c}\right) \qquad (19)$$

In the high-temperature limit $\omega_S{}^2\tau_c{}^2 \ll 1$, and $(T_{2P}\cdot P_M)^{-1}$ should decrease as the temperature decreases, then vary slowly with temperature when $\omega_S{}^2\tau_c{}^2 \approx 1$, and finally $(T_{2P}P_M)^{-1}$ should increase as the temperature decreases further when $\omega_S{}^2\tau_c{}^2 \gg 1$. The results might be explained by assuming that the latter condition is approached in the lower temperature region in water. However, calculations indicate that, assuming reasonable values of 3.5–4.0 kcal mol^{-1} for the apparent activation energy of τ_c, it is not possible to have both the low-temperature and intermediate cases within the narrow liquid range of water. This is especially true at 100 MHz since at this frequency $\omega_S{}^2\tau_c{}^2$ must be significantly greater than 1 if it is also greater than 1 at 60 MHz.

Considerations similar to those above do provide an explanation for the higher apparent values of E_M at 100 MHz than at 60 MHz. At 100 MHz the system is closer to the limit $\omega_S{}^2\tau_c{}^2 > 1$ and therefore E_M will be closer to the value expected for the activation energy for τ_c, 3.9 kcal mol^{-1} in water and 2.5 kcal mol^{-1} in DMF.

Discussion

The kinetic parameters for the systems studied here and several analogous systems are collected in Table IV.

TABLE IV

WATER AND DMF EXCHANGE RATES ON NICKEL(II) COMPLEXES

Complex	Solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	k(25°), sec^{-1}
$NiCR(DMF)_2^{2+}$	DMF	9.5	2.2	1.9×10^6
$NiCRCH_3(DMF)_2^{2+}$	DMF	7.8	−2.9	2.8×10^6
$Ni(DMF)_6^{2+}$ [a]	DMF	15.0	8	3.8×10^3
$NiCR(OH_2)_2^{2+}$	H_2O	6.8	−14.4	4.5×10^4
$NiCR(CH_3)(OH_2)_2^{2+}$	H_2O	6.3	(−15.8)[b]	(5.2×10^4)[b]
$Ni(OH_2)_6^{2+}$ [c]	H_2O	12.1	2.6	3.2×10^4

[a] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966). [b] Values estimated with an assumed hyperfine coupling constant of −1.48 × 10^6 radians sec^{-1}. [c] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

Comparison of the various systems in DMF indicates that the solvent exchange rate at 25° is greater by ~10^3 for the Schiff base complexes. The greater rate is largely due to the $\Delta H^{\ddagger}$ being lower by 6–7 kcal mol^{-1}. This would be consistent with a dissociative mechanism if steric interactions in the Schiff base complexes tend to weaken the solvent–metal ion interaction.

Similar arguments might be applied when considering the $\Delta H^{\ddagger}$ values for the aqueous systems. However now the exchange rate is not greatly different because of a much less favorable $\Delta S^{\ddagger}$ in the Schiff base systems. In fact the very negative $\Delta S^{\ddagger}$ values are unusual for solvent exchange rates in nickel(II) and might indicate that some other mechanism is operative.[17–19] Unfortunately there is a large uncertainty in these $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values because the T_{2M}^{-1} and $\tau_m\Delta\omega_M{}^2$ regions in Figures 5 and 7 are not independently well defined.

It should be noted that the solvent exchange mechanism could be coupled to the diamagnetic–paramagnetic equilibrium if these systems are described by

$$\begin{tikzcd}
\text{S–P–S}^* \arrow[r, shift left, "\tau_{31}"] \arrow[d, shift right, "\tau_{32}"'] & \text{S–P–S} + \text{S}^* \arrow[l, shift left, "\tau_{13}"] \\
\text{S–D–S}^* \arrow[u, shift right, "\tau_{23}"'] \arrow[r, shift left, "\tau_{21}"] & \text{D} + \text{S} + \text{S}^* \arrow[l, shift left, "\tau_{12}"]
\end{tikzcd}$$

---

[16] N. S. Angerman and R. B. Jordan, *J. Chem. Phys.*, **54**, 837 (1971).

[17] A referee has suggested that proton exchange *via* an aquo–hydroxy equilibrium might explain these results. This seems unlikely since the pK_a of $Ni(OH)_2)_6^{2+}$ is certainly >8 (ref 18) and proton exchange should have a rate constant of $\leq 10^2$ sec^{-1}. The latter is consistent with the failure of Swift and Stephenson[19] to observe this type of proton exchange for $Ni(OH_2)_6^{2+}$. Amine substitution generally increases the pK_a of a coordinated water molecule; therefore the proton exchange rate constant should be $<10^2$ sec^{-1} for $Ni(CR)(OH_2)_2^{2+}$.

[18] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 32.

[19] T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1110 (1966).

where S–P–S and S–D–S refer to the solvated paramagnetic and diamagnetic forms, respectively. This may be treated as a three-site problem[20] with bulk solvent as site 1, S–D–S* as site 2, and S–P–S as site 3. The τ_{31}, τ_{13} reaction would be the normal exchange path. If it is assumed that $\tau_{21}^{-1} \gg \tau_{23}^{-1}$, *i.e.*, that desolvation of the diamagnetic species is faster than its conversion to the paramagnetic form, and that the chemical shift in the diamagnetic form, $\Delta\omega_2$, is $\ll \Delta\omega_3$, then

$$(T_{2\mathrm{P}}P_{\mathrm{M}})^{-1} = \frac{\left(\frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right)\left[\frac{1}{T_{23}^{2}} + \frac{1}{T_{23}}\left(\frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right) + \Delta\omega_3^{2}\right]}{\left(\frac{1}{T_{23}} + \frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right)^{2} + \Delta\omega_3^{2}}$$

It can be seen by comparison to eq 4 that the effective exchange lifetime $\tau_{\mathrm{M}}^{-1} = \tau_{32}^{-1} + \tau_{31}^{-1}$. Therefore the solvent exchange rate will be controlled by whichever process is faster, either direct exchange (τ_{31}^{-1}) or the S–P–S to S–D–S conversion (τ_{32}^{-1}). Unfortunately no rate constants are available for the latter process; however Wilkins, *et al.*,[21] have given a lower limit of 10^5 sec^{-1} for this interconversion in Ni(trien)$^{2+}$ and Ni(2,3,2-tet)$^{2+}$ in aqueous solution. It has also been found that tetrahedral–planar interconversions of nickel(II) complexes have rate constants in the range 10^5–10^6 sec^{-1}.[22,23] Although the latter process is not really comparable to that observed here, it appears that structural and spin state changes have rate constants of this order of magnitude.

Other reaction paths are also possible such as

$$\text{S–P–S} \rightleftarrows \text{SP} + \text{S} \rightleftarrows \text{D} + 2\text{S}$$

or

$$\text{S–P–S} \rightleftarrows \text{SD} + \text{S} \rightleftarrows \text{D} + 2\text{S}$$

In these the solvent exchange rate will be controlled by the first reaction and S–P or S–D could be intermediates for the solvent exchange and spin state change. In the second reaction the solvent exchange and spin state change would proceed at the same rate and the solvent exchange rate might be expected to be unusual compared to a purely paramagnetic system. In the absence of rate data for the diamagnetic–paramagnetic change it is not possible to decide between these various possibilities.

---

[20] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 1824 (1969).

[21] R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

[22] L. H. Pignolet, W. DeW. Horrocks, and R. H. Holm, *ibid.*, **92**, 1855 (1970).

[23] G. N. LaMar and E. O. Sherman, *ibid.*, **92**, 2691 (1970).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Kinetic Study of the Complexing of Nickel(II) by Imidazole, Histidine, and Histidine Methyl Ester

BY J. E. LETTER, JR., AND R. B. JORDAN*

Received May 17, 1971

The rate constants for complexation of nickel(II) by imidazole, histidine, and histidine methyl ester have been measured at 23.7° in the pH range 5.6–6.9 and ionic strength 0.1 *M* (KNO$_3$). For imidazole the protonated ($k = 400\ M^{-1}$ sec^{-1}) and neutral ($k = 3.2 \times 10^3\ M^{-1}$ sec^{-1}) forms of the ligand are found to react. Histidine is observed to react only through the neutral form ($k = 2.2 \times 10^3\ M^{-1}$ sec^{-1}), in which one proton is removed from the imidazole group. Reaction is observed for histidine methyl ester both as the monocation ($k = 600\ M^{-1}$ sec^{-1}) with the imidazole proton removed and as the neutral molecule ($k = 2.6 \times 10^3\ M^{-1}$ sec^{-1}) in which both the amino and imidazole protons are removed. The results are consistent with a mechanism in which the imidazole part of the histidine derivatives complexes first with the rate constants showing the expected variation with ligand charge. A second slower reaction is observed in the two histidine systems. This is attributed to the formation of some dinickel species by complexing at the pyrrole nitrogen of the coordinated imidazole part of the histidine ligand.

Introduction

The histidine molecule is a potentially tridendate ligand in aqueous solution, having three different possible bonding sites, *i.e.*, an amino nitrogen, an imidazole nitrogen, and a carboxyl oxygen. Almost every combination of bonding sites has been proposed for the copper(II)–histidine system, but the calorimetric work of Meyer and Bauman[1] indicates binding through the amino and imidazole nitrogens. This is also consistent with the spectrophotometric and CD work of Martin, *et al.*[2] A temperature-jump study[3] of the copper–histidine system showed that only monoprotonated histidine was reactive in the pH range 2.5–4.0 but the complexing sequence could not be determined.

The thermodynamic parameters for the nickel(II)–histidine system have been measured recently by Williams.[4] The recent and previous work generally agree that histidine forms tridentate nickel(II) complexes and the X-ray structure[5] of bis(L-histidino)nickel(II) substantiates this conclusion.

In the hope of establishing the sequence of binding steps in the nickel(II)–histidine system we have studied the kinetics of the reaction of nickel(II) with histidine, histidine methyl ester, and imidazole. The rates of

---

[1] J. L. Meyer and J. E. Bauman, Jr., *J. Amer. Chem. Soc.*, **92**, 4210 (1970).

[2] E. W. Wilson, M. H. Kasperian, and R. B. Martin, *ibid.*, **92**, 5365 (1970).

[3] W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *ibid.*, **91**, 4083 (1969).

[4] D. R. Williams, *J. Chem. Soc.*, 1550 (1970).

[5] K. A. Fraser, H. A. Long, R. Candlin, and M. M. Harding, *Chem. Commun.*, 344 (1965).